

Additional Surface Conductance of the Weakly Charged Porous Surface Layer of a Colloidal Particle

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Abstract – Additional surface conductance is the excess of total surface conductance over the conductance of a diffuse electrical double layer. Theoretical estimation of this value is based on the notion of the porous layer of a colloidal particle. The charge of the porous layer is described by the Stern–Langmuir isotherm. Specific calculations have been made for the particular case of the low Donnan potential of the gel layer. It was established that interfacial potential difference is mostly localized in a medium (gel or solution) where screening is less effective. This fact is responsible for the possible appearance of a maximum at the concentration dependence of a ζ -potential. In this case, additional surface conductance exceeds Bikerman's conductance: the pattern of the concentration dependence in the first case is governed by the coverage of adsorption sites for potential-determining ions.

INTRODUCTION

Interpretation of surface conductance has interested researchers for many years, because measurements of surface conductance could offer information on the spatial structure of the electrical double layer. These measurements make it possible to look over the smooth surface of electrokinetic slipping and to understand the mechanism of the development of electrokinetic potential; in other words, they allow us to further develop a quantitative description of the surface of hydrosols [1, 2]. Although the importance of investigation into surface conductance is well understood, it should be noted that studies on modeling the surface conductance lag behind experimental and theoretical works at the phenomenological level, where surface conductance is regarded as an integral parameter of the surface layer.

In general, the surface conductance of the colloidal particle K_s may be presented as a sum of the surface conductance of the diffuse part of the electrical double layer (denoted also as the Bikerman part of the surface conductance [3]) K_{SB} and excessive or additional surface conductance K_{SA} :

$$K_s = K_{SA} + K_{SB},$$

$$K_{SB} = \frac{2F^2 C}{RT\kappa_b} (D^+ (e^{-\zeta/2} - 1) + D^- (e^{\zeta/2} - 1)), \quad (1)$$

where $\kappa_b = \sqrt{\frac{8\pi F^2 C}{\epsilon_b RT}}$ is the inverse Debye radius in electrolyte solution, ϵ_b is the solution permittivity, D^\pm is the diffusion coefficient of cations and anions, and ζ is the dimensionless electrokinetic potential (hereafter the

dimensionless potential, related with dimensional parameter $\tilde{\zeta}$ by the relationship $\zeta = F\tilde{\zeta}/RT$, will be used).

Bikerman's mechanism is not universal and common for colloidal particles of any nature. When an experimental value of surface conductance exceeds K_{SB} , additional surface conductance is to be introduced and a hypothesis regarding its nature should be put forward.

One of the promising models of additional surface conductance is based on the notion of the mobility of the adsorbed ions within the Stern layer. In this case, some researchers [4, 5] proceed from the ion monolayer, and others [6, 7] – from the layer of some finite thickness (the gel layer or surface layer), where the adsorption sites are distributed with a certain density. Some authors believe that only definite types of the adsorbed ions may acquire mobility, while other ones suggest mobility of both coions (potential-determining ions) and counterions. Yet other authors [4] assume that this mobility is confined only by the displacement of the ions across the particle surface (exchange of the adsorbed ions with the bulk ions is negligibly small); the others [8, 9] are of the opinion that adsorbed ions may be freely exchanged with the bulk ions.

The diversity of these assumptions may be integrated within the framework of one multiparametric model of the additional surface conductance. Constitutive parts of this model are: a spatially homogeneous surface layer of finite thickness; an equation of the Langmuir–Stern adsorption isotherm for ions of any type; and finite diffusion coefficients for all types of ions within the surface layer.

Versatile possibilities, inherent to this model, require substantial efforts in order for further develop-

ment to be made. Different versions of this model were especially successful when applied to electroosmosis and electrophoresis [10 - 12] (in particular, when modelling electrokinetic behavior of the particles covered by the adsorbed layer of a polyelectrolyte). However, so far, attention was focused on the subsets of this model discussed above; recently, this problem has been examined in its general form [13], and it has been demonstrated, for example, that there is no crucial difference between the monolayer and a sufficiently thin gel layer.

The aim of this work was to study the model of the additional surface conductance described above, as applied to the specific case of low potentials of the gel layer. This case is of interest for both the development of the theory (since it provides for the elucidation of the dependence of additional surface conductance on gel layer thickness and adsorption parameters), and its application (especially if one takes into account that the surface of many biocolloids, such as cells, is covered by glycocalyx (weakly dissociating ionite)).

ADSORPTION EQUATION AND THE DONNAN POTENTIAL

Consider an electrolyte of arbitrary composition containing ions with charges z_i (z_i is positive for cations and negative for anions) of the concentrations C_i ($i = 1, \dots, N$, N is the number of types of ions). A plane porous layer with thickness H , covering the particle impermeable for ions, is in equilibrium with this solution. The ions may be adsorbed on the porous layer according to the following equation [14]:

$$A_i = \frac{Q_i K_i C_i e^{-z_i \Psi}}{1 + K_i C_i e^{-z_i \Psi}}, \quad (2)$$

where K_i is a constant of the adsorption affinity of the i th ion, Q_i is the concentration of the adsorption sites for the i th ion, and Ψ is the electrical potential.

The physical process, described by this equation, implies that the potential of the gel layer is governed by the ions with much higher adsorption affinity (by potential-determining ions). Potential, arising from this effect at the adsorption equilibrium, prevents further adsorption of potential-determining ions and promotes adsorption of the oppositely charged ions (in solution, these are counterions). Equilibrium inside of a sufficiently thick gel layer will be achieved when the potential acquires such a value that net density charges of positive and negative ions become equal, and the volume of the gel will be electroneutral. This value of the potential is known as the Donnan potential Ψ_D ; it may be determined from the equation:

$$\sum_{i=1}^N z_i A_i(\Psi_D) = 0, \quad (3)$$

and is solely dependent on the adsorption parameters of the gel.

For the simplest case of $N = 2$, $z_1 = +1$, $z_2 = -1$, equation (3) has a simple analytical solution. Rewrite this equation in the form

$$\frac{Q^+ K^+ e^{-\Psi_D}}{1 + K^+ C e^{-\Psi_D}} - \frac{Q^- K^- e^{\Psi_D}}{1 + K^- C e^{\Psi_D}} = 0,$$

and substitute $x = e^{\Psi_D}$:

$$\frac{Q^+ K^+}{x(1 + K^+ C/x)} = \frac{Q^- K^- x}{1 + K^- C x}.$$

The latter equation is reduced to a quadratic equation with respect to x :

$$x^2 + x \frac{K^+ C (Q^- - Q^+)}{Q^-} - \frac{K^+ Q^+}{K^- Q^-} = 0. \quad (4)$$

It is easy to see that at $Q^+ = Q^-$,

$$x = \sqrt{K^+ / K^-}, \quad (5)$$

from which follows that the root of equation (4) having physical meaning is

$$x = \frac{K^+ C (Q^+ - Q^-)}{2Q^-} + \sqrt{\frac{K^{+2} C^2 (Q^+ - Q^-)^2}{4Q^{-2}} + \frac{K^+ Q^+}{K^- Q^-}}. \quad (6)$$

Thus, we recognized that, when adsorption capacities for cations and anions are equal, the Donnan potential is a constant value determined only by the ratio between adsorption affinities, and is independent of the electrolyte concentration. Consider, then, more complicated cases. Assume, for definiteness sake, that $K^+ > K^- > 1$. Figure 1 shows the concentration dependence of Ψ_D . It might be well to point out that the patterns of all the curves are different within two distinct regions: at $K^+ C < 1$ Ψ_D they are virtually independent of the concentration, whereas at $K^+ C > 1$ this dependence takes place. At low concentrations, when adsorption is far from saturation, both cations and anions may be adsorbed unlimitedly, and the difference in capacities results only in the constancy of Ψ_D and redefinition of the affinities entering into equation (5):

$$e^{\Psi_D} = \sqrt{\frac{K^+ Q^+}{K^- Q^-}}. \quad (7)$$

At higher concentrations, when coverage of the adsorption sites cannot be considered as low, Ψ_D increases with increasing concentration (when the capacity with respect to cations is higher than that with respect to anions), and decreases in the opposite case. At $Q^+ < Q^-$, adsorption of anions increases up to saturation with the

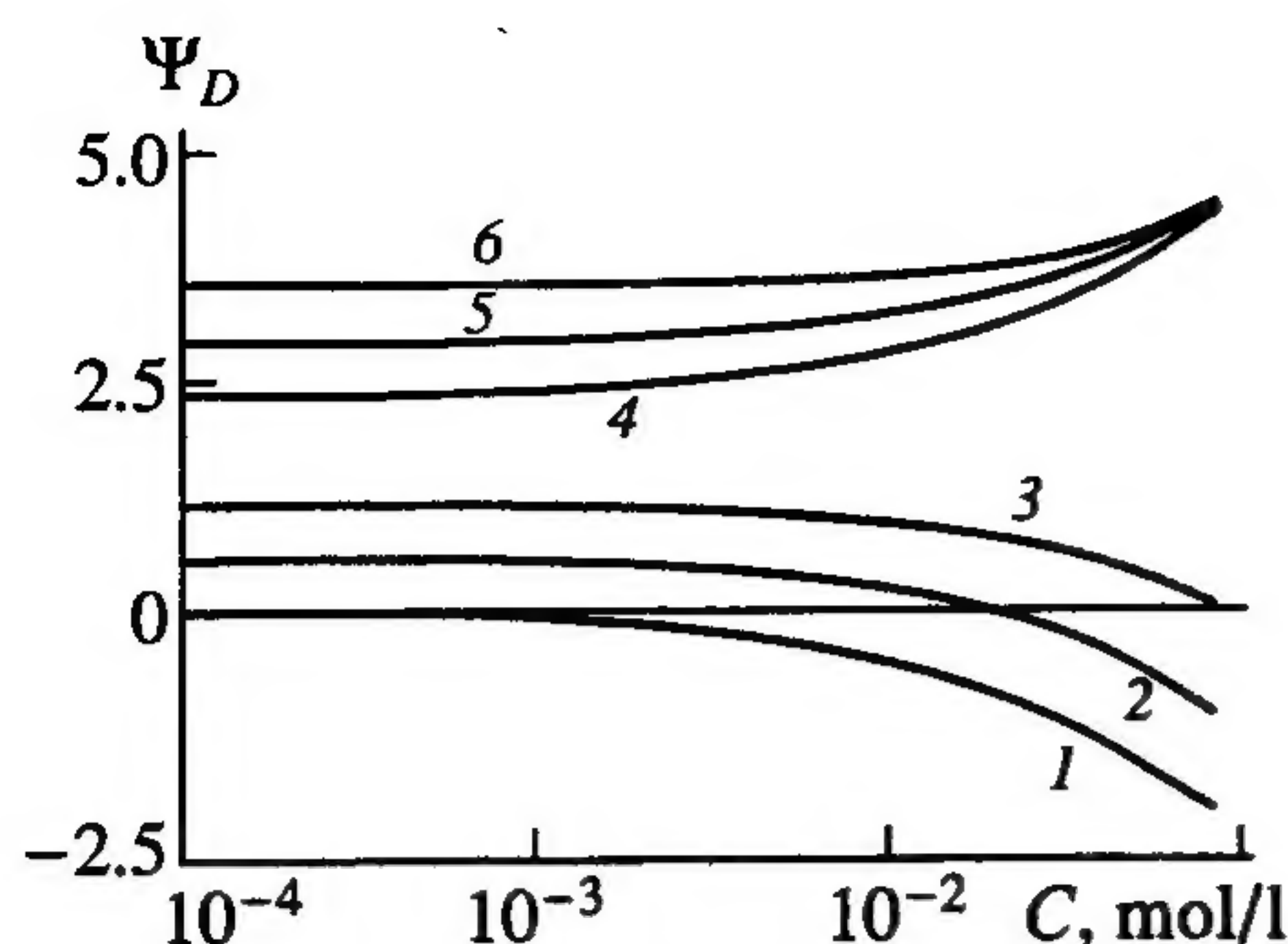


Fig. 1. Dependence of the Donnan potential of the gel layer Ψ_D on the electrolyte concentration: for Q^- (1 - 3) 0.1, (4 - 6) 0.001 mol/l; for K^- (1, 4) 10, (2, 5) 3.3, (3, 6) 1 l/mol. $Q^+ = 0.01$ mol/l; $K^+ = 100$ l/mol.

increase in Ψ_D , whereas adsorption of cations remains far from saturation. At this point, the potential should be increased to provide for the electroneutrality and to prevent further adsorption of cations. At $Q^- > Q^+$, adsorption of cations achieved the saturation point; to prevent unlimited adsorption of anions, the potential should be lowered to the point of the reversal of charge.

Figure 2 demonstrates the dependence of Ψ_D on the absolute values of cation affinities at the constant ratio of the affinities. The conclusion drawn from Fig. 1 is fully valid: the range of constant Ψ_D decreases in approximate agreement with the displacement of the boundary $CK^+ = 1$.

SPATIAL POTENTIAL DISTRIBUTION WITHIN THE GEL LAYER

To calculate the spatial distribution of the potential, we should solve the Poisson-Boltzmann equation for the solution (at $x < 0$, potential Ψ_1) and for the gel (at $0 < x < H\Psi_2$):

$$\frac{d^2\Psi_2}{dx^2} = -\frac{4\pi F^2}{\varepsilon_g RT} \sum_{i=1}^N z_i A_i(\Psi_2). \quad (8)$$

A sufficient condition for low gel charge (and for applicability of the Debye approximation) is the inequality $|\Psi_D| < 1$, since all potentials in a system do not exceed the Donnan potential. However, to derive the Debye equation for the gel, one may use substitution $\Psi_2 = \Psi_D + \Psi_3$ and the less rigorous condition $\Psi_3 < 1$. Expanding the right-hand term of equation (8) at the point $\Psi = \Psi_D$, we obtain the analog of the Debye equation

$$\frac{d^2\Psi_3}{dx^2} = \kappa_g^2 \Psi_3, \quad (9)$$

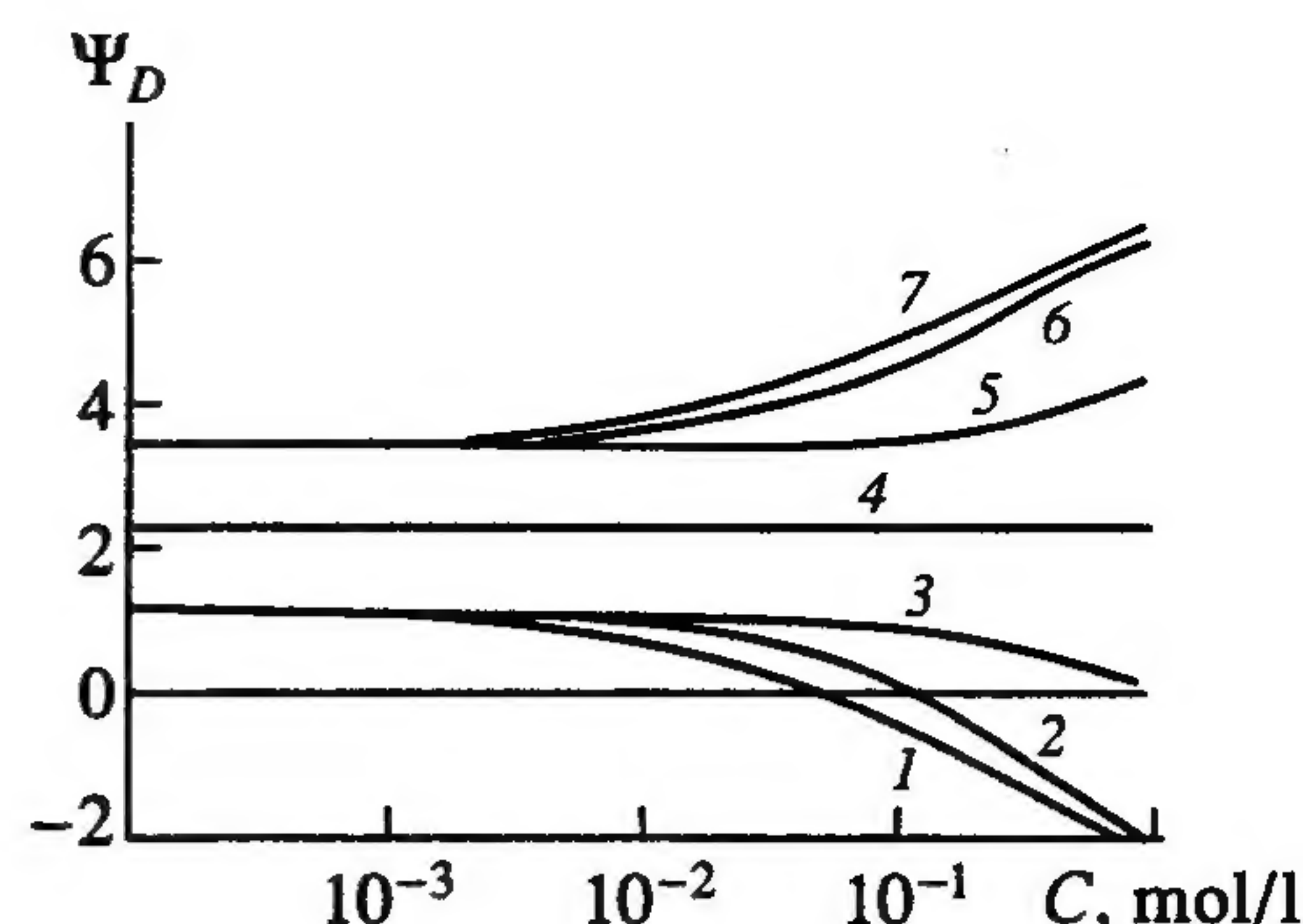


Fig. 2. Dependence of the Donnan potential of the gel layer Ψ_D on the electrolyte concentration: for Q^- (1 - 3) 0.1, (4) 0.01, (5 - 7) 0.001 mol/l; for K^+ (1, 7) 1000, (2, 6) 100, (3, 5) 10 l/mol. $Q^+ = 0.01$ mol/l; $K^- = K^+/100$.

where κ_g , the inverse screening radius in the gel, is given by the expression

$$\kappa_g^2 = \frac{2\pi F^2}{\varepsilon_g RT} \times \sum_{i=1}^N \frac{z_i^2 Q_i K_i C_i e^{-z_i \Psi_D} (1 + 2K_i C_i e^{z_i \Psi_D})}{(1 + K_i C_i e^{-z_i \Psi_D})^2}. \quad (10)$$

The Debye equation for the solution has its common form

$$\frac{d^2\Psi_1}{dx^2} = \kappa_b^2 \Psi_1. \quad (11)$$

Solutions of equations (9) and (11) of the type

$$\begin{aligned} \Psi_1 &= A_1 e^{\kappa_b x} + B_1 e^{-\kappa_b x}, \\ \Psi_3 &= A_3 e^{\kappa_g x} + B_3 e^{-\kappa_g x} \end{aligned} \quad (12)$$

should comply with the boundary conditions:

$$\Psi_1|_{x \rightarrow -\infty} = 0$$

is the electroneutrality of the bulk solution;

$$\Psi_1|_{x=0} = (\Psi_D + \Psi_3)|_{x=0}$$

is the continuity of the potential at the solution-gel interface;

$$\varepsilon_b \frac{d\Psi_1}{dx} \Big|_{x=0} = \varepsilon_g \frac{d\Psi_3}{dx} \Big|_{x=0}$$

is the continuity of induction at the solution-gel interface;

$$\frac{d\Psi_3}{dx} \Big|_{x=H} = 0$$

is the absence of the surface charge at the gel–solid interface. Accounting for these conditions, the coefficients in equation (12) are equal to

$$B_1 = 0; \quad A_1 = \Psi_D + A_3 + B_3,$$

$$A_3 = -\frac{\mu \Psi_D e^{-2\kappa_g H}}{1 + \mu - (1 - \mu) e^{-2\kappa_g H}},$$

$$B_3 = -\frac{\mu \Psi_D}{1 + \mu - (1 - \mu) e^{-2\kappa_g H}},$$

where μ is the parameter characterizing relative screening efficiency in the solution and gel:

$$\mu = \frac{\epsilon_b \kappa_b}{\epsilon_g \kappa_g},$$

and the potential at the gel–solution interface (ζ -potential) is

$$\zeta = \frac{\Psi_D (1 - e^{-2\kappa_g H})}{1 + \mu - (1 - \mu) e^{-2\kappa_g H}}. \quad (13)$$

Hence, it was established that the ζ -potential of the system considered does not correlate directly with the adsorption parameters of the gel: these parameters only appear in the expressions for the Donnan potential and for screening radius in the gel. This is a distinctive feature of the Debye approximation; no such distinction exists at arbitrary values of the potential in the gel layer. Figure 3 shows the dependence of ζ -potential on its controlling parameters. It can be seen that ζ -potential increases with increasing gel layer thickness, reaching its maximal value at $\kappa_g H > 5$:

$$\zeta = \frac{\Psi_D}{1 + \mu}.$$

At small μ , corresponding to low concentrations in a solution, ζ -potential is close to the Donnan potential, the potential difference being mostly localized in a solution. At higher μ , corresponding to higher concentrations, ζ -potential is sharply reduced, the potential drop being mainly displaced to the gel region. Thus, it may be concluded that the potential difference is mainly localized in a medium where screening is poorly exhibited.

SURFACE CONDUCTANCE OF A WEAKLY CHARGED GEL

After calculation of the spatial distribution of a potential in the surface layer, we may express the additional surface conductance in integral form:

$$K_{SA} = \frac{F^2}{RT} \sum_{i=1}^N z_i^2 D_{iS} \int_0^H A_i(x) dx, \quad (14)$$

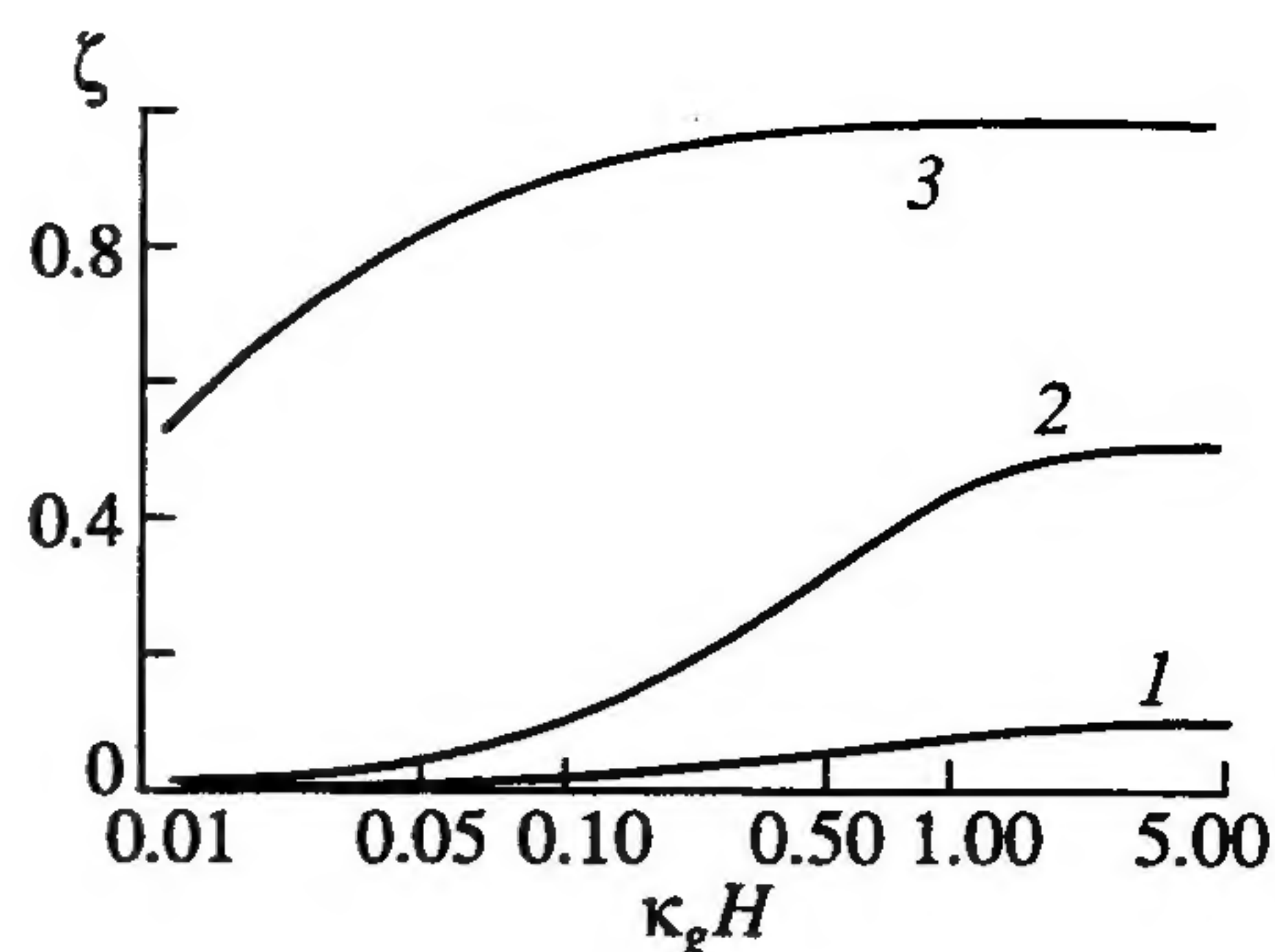


Fig. 3. Dependence of the ζ -potential of the gel layer on the dimensionless thickness of the layer $\kappa_g H$ and efficiency screening parameter μ . $\Psi_D = 1$; $\mu = (1) 10$, $(2) 1$, $(3) 0.1$.

which may be easily solved by expanding the integrand over the potential power and by making use of the explicit dependence of the potential on the coordinate. The final result may be presented as

$$K_{SA} = \frac{F^2}{RT} H \sum_{i=1}^N \frac{z_i^2 Q_i K_i C_i D_{iS}}{1 + K_i C_i} \left[1 - \frac{z_i K_i C_i \Psi_D}{1 + K_i C_i} \times \left(1 - \frac{\mu (1 - e^{-2\kappa_g H})}{\kappa_g H (1 + \mu - (1 - \mu) e^{-2\kappa_g H})} \right) \right]. \quad (15)$$

Let us analyze this expression for one set of parameters: $\epsilon_b = 80$, $\epsilon_g = 10$, $D_S^+ = D_S^- = 0.1D$, $Q^+ = Q^- = 0.01$ mol/l; $K^+ = 100$ l/mol; $K^- = 1$ and 10 l/mol; $H = 1$ and 10 Å, and the electrolyte is KCl. The dependences of K_{SA} and K_{SB} on the concentration are shown in Figs. 4a and 4b. Note the following specific properties: both components of the surface conductance become greater with increasing thickness of the surface layer, the Bikerman conductance increasing much faster than the additional surface conductance. Both components are characterized by two distinct parts of the concentration dependence: within the range of $0.01 - 0.1$ mol/l rapid growth is changed by a slightly expressed dependence. As expected for a weakly charged system, additional surface conductance is higher than the Bikerman conductance. Consider the concentration dependences of the ζ -potential (Fig. 5) and the parameter μ (Fig. 6) to explain the behavior of the additional surface conductance. Curves plotted on these figures have two distinct parts: at low concentrations, μ is independent of C (the screening radii in both solution and gel vary to the same extent), however, at higher concentrations, the screening in a solution becomes more marked (adsorption sites in the gel are mostly covered), and in accordance with the conclusions made in the previous section, the potential difference is displaced mainly to the gel. This potential drop displacement affects the concentration dependence of the ζ -potential being depicted as the descending part of the curve (note that such a

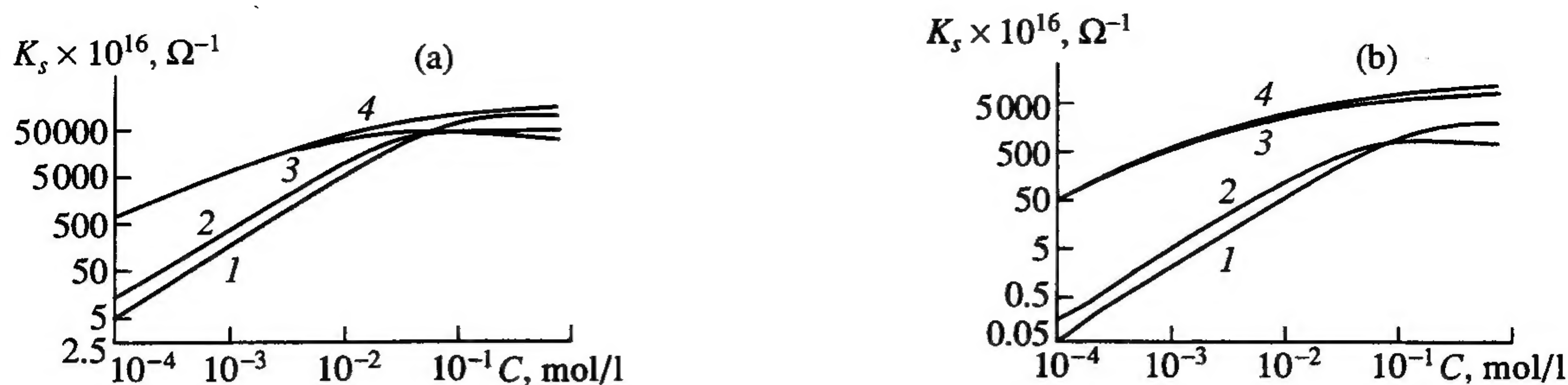


Fig. 4. Dependence of (1, 2) the Bikerman and (3, 4) the additional surface conductance on the electrolyte concentration: for K^- (1, 3) 1, (2, 4) 10 l/mol; for H (a) 10, (b) 1 Å. $Q^+ = Q^- = 0.01$ mol/l; $K^+ = 100$ l/mol.

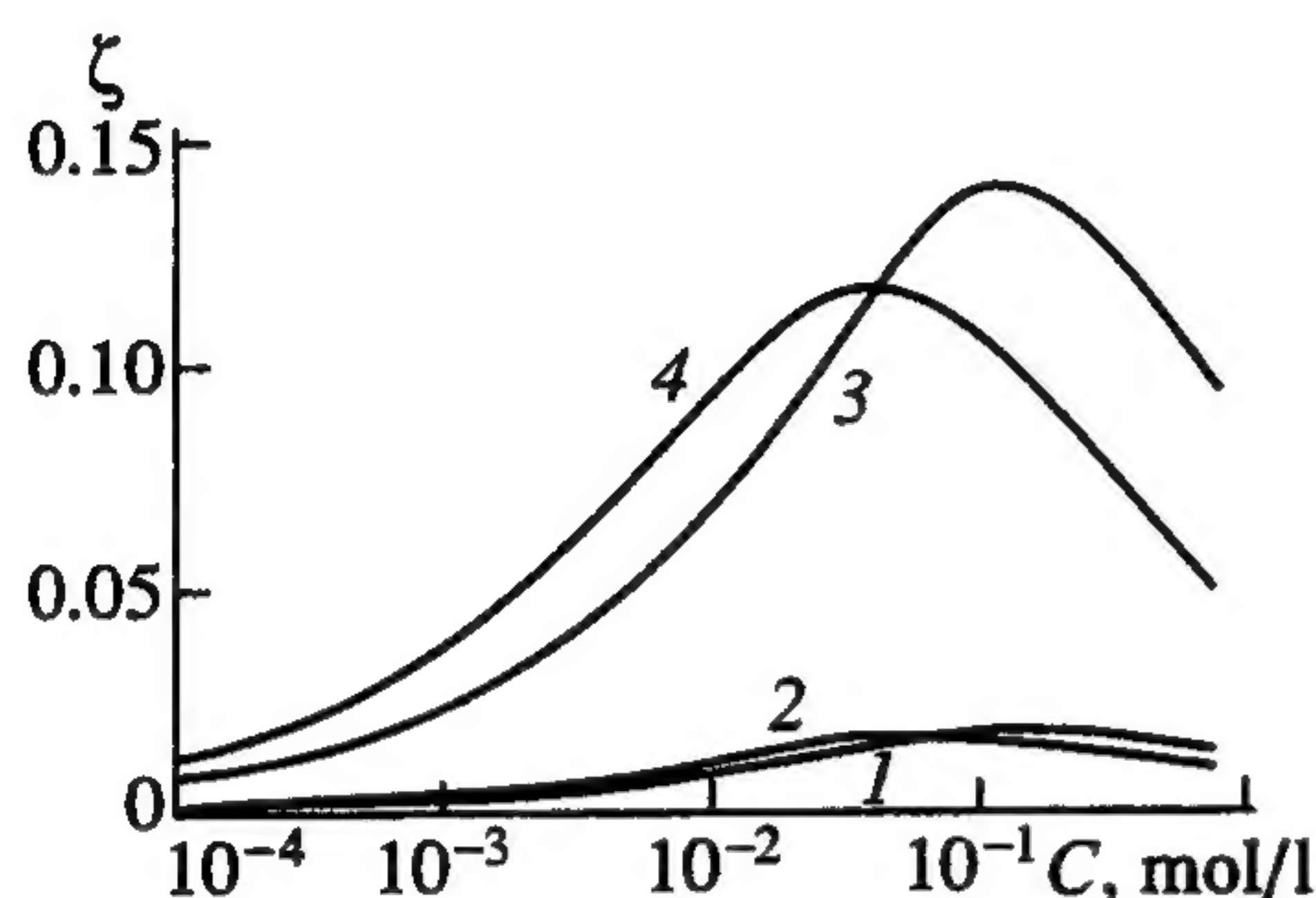


Fig. 5. Dependence of the ζ -potential of the gel layer on the electrolyte concentration: for K^- (1, 3) 1, (2, 4) 10 l/mol; for H (1, 2) 1, (3, 4) 10 Å. $Q^+ = Q^- = 0.01$ mol/l; $K^+ = 100$ l/mol.

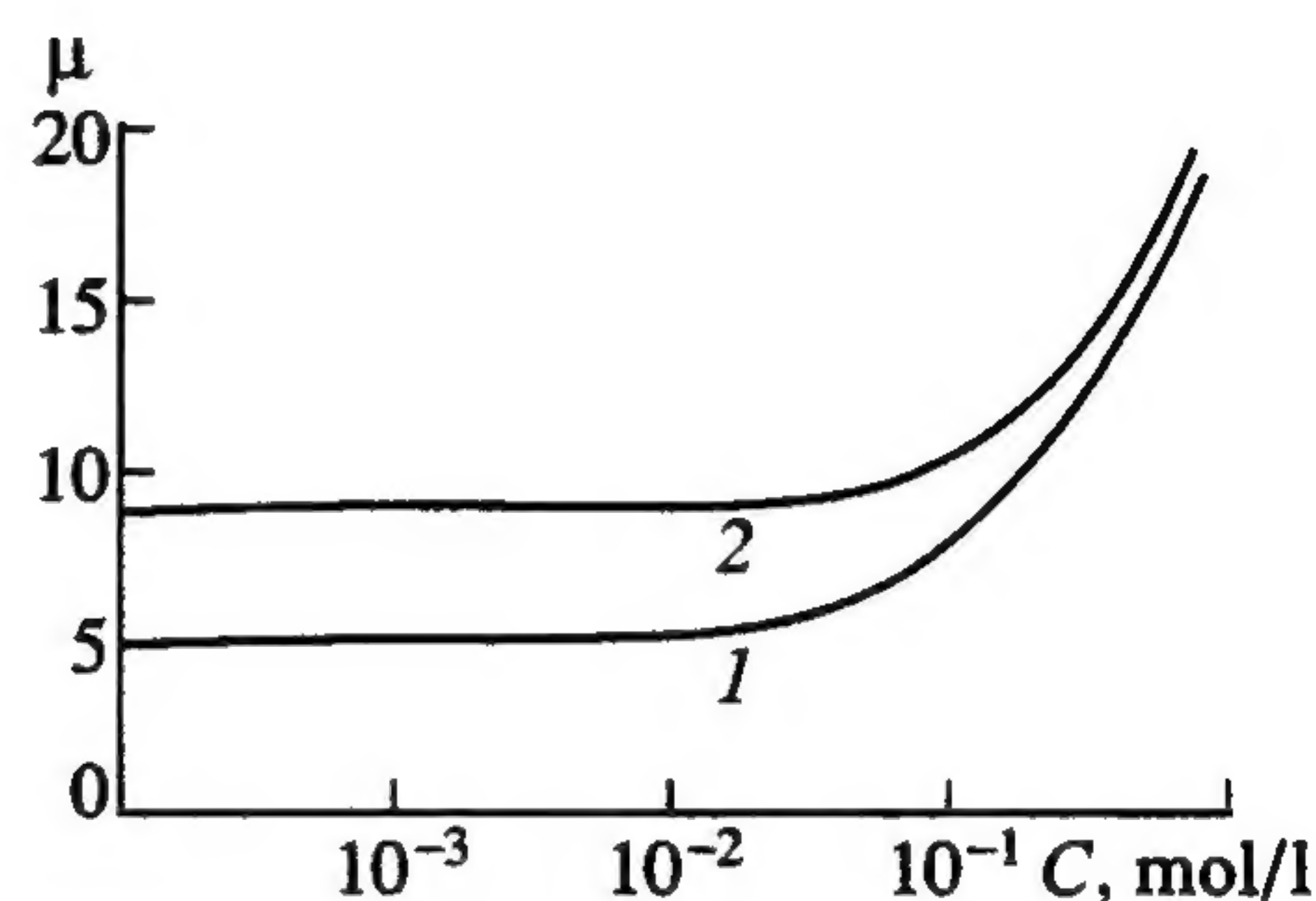


Fig. 6. Dependence of the screening efficiency parameter μ on the electrolyte concentration: for K^- (1) 10, (2) 1 l/mol. $Q^+ = Q^- = 0.01$ mol/l; $K^+ = 100$ l/mol.

drop in the ζ -potential is not reported for the earlier discussed models of both thin surface layer and monolayer [9]). If the concentration dependence of the additional surface conductance is first and foremost related to the variation both in the coverage of the adsorption sites and in the spatial distribution of the potential, then yet another important factor – the concentration dependence of the ζ -potential – should be taken into account when dealing with the Bikerman surface conductance. The main parameter governing the concentration dependence of all the parameters involved in the model considered is the coverage of the adsorption sites for the potential-determining ions.

Strong dependence of the ζ -potential and surface conductance on the concentration is associated with the fact that, in this particular case, there are no foreign ions in the system under investigation. When only one type of potential-determining ion is present in a solution, a decrease in the electrolyte concentration results in unlimited decreases in adsorption, charge and potential. Addition of ions of the third and subsequent types to the system is revealed in a less pronounced effect of the charge variation with electrolyte concentration.

Strong concentration dependence of the surface conductance is helpful in order to distinguish experimentally between the model of the porous surface layer and any other possible models. In addition, the relatively high sensitivity of the surface conductance to the parameters of the porous layer makes it possible to

determine the latter. We believe that these factors validate the measurement of the concentration dependence of the surface conductance.

The porosity of the capillary walls of nuclear track filters, similar to the porous glasses [15], was recently reported [16].

ADDITIONAL SURFACE CONDUCTANCE OF THE ADSORBED LAYERS OF POLYELECTROLYTES

As was mentioned above in connection with Donath [10, 11] and Oshima [12], and with recently reported data [17], the theory under discussion may be applied successfully to the adsorbed layers of polyelectrolytes with regard for possible adsorbent porosity. An important example of this application is microcrystalline cellulose, where the significant role of electrostatic interaction during adsorption was proven [17]. Since the pH and concentration of electrolyte were varied in these experiments independently, the equations, suggested above for systems containing at least three types of ions, should be defined more clearly. It may be assumed that in the case of polyelectrolytes, surface layers are thicker (up to tens of angstroms) and more impermeable for ions, and that the charge is established in accordance with equation (2). These layers are clearly distinguished by their inhomogeneity over the thickness: a compact thin layer of macromolecules with many seg-

ments attached to the surface is, in general, adjacent to the surface; loops and tails of polymer chains, attached to the surface with just a few segments, are extended into the solution at a far greater distance from the surface. Within the framework of the discussed model, these features should be depicted as the dependences of the density of adsorption sites Q_i on the distance to the solid surface. A similar dependence can probably also be assumed for the diffusion coefficients of ions in the adsorbed layer.

To account for the indicated dependences, the extension of the theory developed above acquires no essential difficulties until the Debye approximation may be used to solve the Poisson–Langmuir equation. It might be expected that this approximation be rather realistic for polyelectrolytes with low-acid or low-base ionogenic groups, as well as for ampholytes, since the latter deliberately establish low charge in the vicinity of the zero charge point. More extensive investigation of the surface conductance of the adsorbed layers of polyelectrolytes may require special study.

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